

Electronic Supporting Information (ESI) for Substituent Effects on the Structure and Supramolecular Assembly of Bis(dioxaborole)s

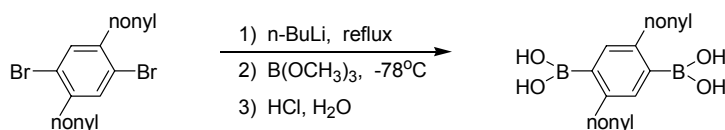
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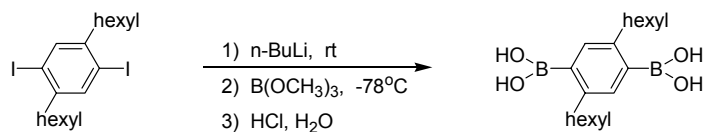
(1) Synthesis and characterization of 2,5-Dinonylbenzene-1,4-diboronic acid from 1,4-Dibromo-2,5-dinonylbenzene (3a):



The synthesis of 2,5-Dinonylbenzene-1,4-diboronic acid from 1,4-Dibromo-2,5-dinonylbenzene is similar to the literature procedure on the synthesis of 2,5-Dihexylbenzene-1,4-diboronic acid.¹ 1,4-Dibromo-2,5-dinonylbenzene (1.3 g, 2.57 mmol) was stirred rapidly in dry, degassed hexane (15 ml) and heated to reflux under Argon. A solution of n-BuLi in hexanes (0.95M, 8.2 ml, 7.8 mmol) was added dropwise to the refluxing solution. The resulting cloudy solution was refluxed for 15 hours. The solution was then cooled to -78°C and neat trimethyl borate (2.93 ml, 25.7 mmol) was added in one portion. The mixture was stirred at room temperature for 11 hours. To the stirring solution, 30 ml of 2M aq. HCl was added and allowed to stir for 3 hours. The hexane was removed under reduced pressure to yield an aqueous solution with an off-white precipitate. This solid was collected by vacuum-filtration and washed by 2M aq. HCl (3 x 25 ml) to yield 0.2571 g of air-dried white powder solid. ¹H NMR of this air-dried white powder showed 90%

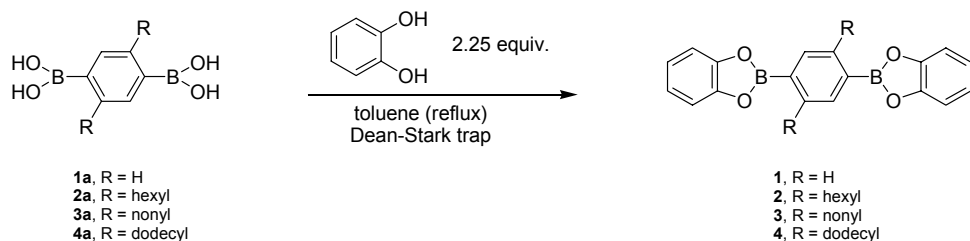
purity (24% isolated yield). ^1H NMR (300 MHz, CD_3OD , δ): 7.07 (s, 2H, Ar-H), 2.56 (t, 4H, J = 7.8 Hz, $\alpha\text{-CH}_2\text{-}$), 1.64-1.44 (m, 4H, $\beta\text{-CH}_2\text{-}$), 1.40-1.16 (m, 24H, $\text{-CH}_2\text{-}$), 0.90 (t, 6H, J = 6.8 Hz, -CH_3). NOTE: refluxing of the reaction system is very important to yield diboronic acids, otherwise, monoboronic acid is the only product formed. .

(2) Synthesis and characterization of 2,5-Dihexylbenzene-1,4-diboronic acid from 1,4-Diiodo-2,5-dihexylbenzene (2a):



To a solution of 1,4-Diiodo-2,5-dihexylbenzene (0.9 g, 1.89 mmol) in dry, degassed hexane (20 ml) at room temperature was added a solution of $n\text{-BuLi}$ in hexanes (0.95M, 6.0 ml, 5.7 mmol). The resulting cloudy solution was stirred at room temperature for 12 hours. The solution was then cooled to -78°C and neat trimethyl borate (2.16 ml, 18.9 mmol) was added in one portion. The cloudy mixture was stirred at -78°C for two hours, warmed to room temperature and stirred for an additional 12 hours. After this time, 30 ml of 2M aq. HCl was added with vigorous stirring and the solution was stirred for 3 more hours. Hexane was removed under reduced pressure to yield an aqueous solution with a white precipitate which was collected by vacuum-filtration and washed with 2M aq. HCl (3 x 25 ml) leaving an off-white solid after air-drying. This solid is suspended in 1M aq. HCl and heated in a warm water bath ($\sim 50\text{-}60^\circ\text{C}$) to remove residual H_3BO_3 . The insoluble product was filtered and air-dried to yield 0.2250 g (36% isolated yield) of 2,5-Dihexylbenzene-1,4-diboronic acid was ($\sim 95\%$ pure by ^1H and ^{11}B NMR). ^1H NMR (300 MHz, CD_3OD , δ): 7.07 (s, 2H, Ar-H), 2.56 (t, 4H, J = 7.7 Hz, $\alpha\text{-CH}_2\text{-}$), 1.62-1.48 (m, 4H, $\beta\text{-CH}_2\text{-}$), 1.40-1.98 (m, 12H, $\text{-CH}_2\text{-}$), 0.90 (t, 6H, J = 6.6 Hz, -CH_3).

(3) Synthesis and characterization of bis(dioxaborole)s 1-4:



(i) Synthesis and characterization of bis(dioxaborole) 1: To a mixture of benzene-1,4-diboronic acid (0.2431 g, 1.467 mmol) and catechol (0.3672 g, 3.335 mmol) 85 ml of toluene was added and the flask fitted with a Dean-Stark apparatus. The resulting solution was refluxed for two days to yield a white cloudy solution. The solution was cooled to room temperature slowly. The solvent was then removed under reduced pressure to form an off-white crystalline solid. This off-white solid was then kept at 115°C under vacuum (~1mmHg, Kugelrohr) for five hours to yield purified **1** (0.4539 g, 99% yield). ^1H NMR (300 MHz, CDCl_3 , δ): 8.21 (s, 4H, Ar-H), 7.35 (dd, 4H, $J = 5.9, 3.3$ Hz), 7.16 (dd, 4H, $J = 6.0, 3.3$ Hz). ^{11}B NMR (160 MHz, CDCl_3 , δ): 32 ppm ($\text{BF}_3\cdot\text{Et}_2\text{O} = 0$ ppm, external reference); Solid ^{11}B NMR (160 MHz, solid state, δ): 18 ppm ($\text{B(OH)}_3 = 14$ ppm, external reference). λ_{abs} : 282 nm ($\epsilon = 2.5 \times 10^4 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, CH_2Cl_2); λ_{Em} : 385 nm (λ_{Ex} : 280 nm, CH_2Cl_2). MS calcd for $\text{C}_{18}\text{H}_{12}\text{B}_2\text{O}_4$: 314.0928; found: m/z 314.0933.

(ii) Synthesis and characterization of bis(dioxaborole) 2: To a mixture of 2,5-Dihexyl-1,4-phenylene diboronic acid (0.1056 g, 0.2781 mmol) and catechol (0.0653 g, 0.5930 mmol) 50 ml of toluene was added and the flask fitted with a Dean-Stark apparatus. The resulting solution was refluxed under argon for 9 hours to yield a slightly cloudy solution. The solution was cooled to room temperature slowly. The solvent was removed under reduced pressure leaving an off-white crystalline solid. The resulting solid was washed by 50 ml of distilled CH_3CN to yield **2** (0.1133 g, 82% yield). ^1H NMR (300 MHz, CDCl_3 , δ): 8.01 (s, 2H, Ar-H), 7.35 (m, 4H, Ar-H), 7.16 (m, 4H, Ar-H), 3.08 (t, 4H, $J = 7.8$ Hz, $\alpha\text{-CH}_2\text{-}$), 1.75-1.62 (m, 4H, $\beta\text{-CH}_2\text{-}$), 1.52-1.24 (m, 12H, $\text{-CH}_2\text{-}$), 0.90 (t, 6H, $J = 7.1$ Hz, -CH_3). ^{11}B NMR (160 MHz, CDCl_3 , δ): 30 ppm ($\text{BF}_3\cdot\text{Et}_2\text{O} = 0$ ppm, external reference); Solid ^{11}B NMR (160 MHz, solid state, δ): 17 ppm ($\text{B(OH)}_3 = 14$ ppm, external reference). λ_{abs} : 281 nm ($\epsilon = 4.3 \times 10^4 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$, CH_2Cl_2); λ_{Em} : 342 nm (λ_{Ex} : 280 nm, CH_2Cl_2). MS calcd for $\text{C}_{30}\text{H}_{36}\text{B}_2\text{O}_4$: 482.2810; found: m/z 482.2809.

(iii) Synthesis and characterization of bis(dioxaborole) 3: To a mixture of 2,5-Dinonyl-1,4-phenylene diboronic acid (0.1163 g, 0.2781 mmol) and catechol (0.0608 g, 0.5522 mmol) in a flask fitted with a Dean-Stark trap, 40 ml of distilled toluene was added. The resulting solution was refluxed under argon for 12 hours to yield a slightly cloudy solution. The solution was cooled to room temperature slowly. The solvent was removed under reduced pressure leaving an off-white crystalline solid. The resulting solid was washed by 50 ml of distilled CH₃CN to yield **3** (0.0952 g, 61% yield). ¹H NMR (300 MHz, CDCl₃, δ): 8.00 (s, 2H, Ar-H), 7.35 (m, 4H, Ar-H), 7.15 (m, 4H, Ar-H), 3.08 (t, 4H, *J* = 8.0 Hz, α-CH₂-), 1.75-1.62 (m, 4H, β-CH₂-), 1.52-1.24 (m, 24H, -CH₂-), 0.87 (t, 6H, *J* = 6.8 Hz, -CH₃). ¹¹B NMR (160 MHz, CDCl₃, δ): 30 ppm (BF₃·Et₂O = 0 ppm, external reference). λ_{abs}: 281 nm (ε = 4.0 × 10⁴ dm³·mol⁻¹·cm⁻¹, CH₂Cl₂); λ_{Em}: 344 nm (λ_{Ex}: 280 nm, CH₂Cl₂). MS calcd for C₃₆H₄₈B₂O₄: 566.3751; found: *m/z* 566.3760.

(iv) Synthesis and characterization of bis(dioxaborole) 4: To a mixture of 2,5-Didodecyl-1,4-phenylene diboronic acid (0.2334 g, 0.4645 mmol) and catechol (0.1098 g, 0.997 mmol) in a flask fitted with a Dean-Stark trap, 55 ml of distilled toluene was added. The resulting solution was refluxed under argon for 24 hours to yield a slightly cloudy solution. The solution was cooled to room temperature slowly. The solvent was removed under reduced pressure leaving an off-white crystalline solid. The resulting solid was washed by 25 ml of distilled CH₃CN to yield **4** (0.1471 g, 49% yield). ¹H NMR (300 MHz, CDCl₃, δ): 8.00 (s, 2H, Ar-H), 7.34 (m, 4H, Ar-H), 7.15 (m, 4H, Ar-H), 3.08 (t, 4H, *J* = 8.0 Hz, α-CH₂-), 1.75-1.62 (m, 4H, β-CH₂-), 1.52-1.20 (m, 36H, -CH₂-), 0.87 (t, 6H, *J* = 6.8 Hz, -CH₃). ¹¹B NMR (160 MHz, CDCl₃, δ): 31 ppm (BF₃·Et₂O = 0 ppm, external reference). λ_{abs}: 281 nm (ε = 3.8 × 10⁴ dm³·mol⁻¹·cm⁻¹, CH₂Cl₂); λ_{Em}: 344 nm (λ_{Ex}: 280 nm, CH₂Cl₂). MS calcd for C₄₂H₆₀B₂O₄: 650.4692; found: *m/z* 650.4684.

1 Rehahn, M.; Schluter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991-2003.